

Ionicly tagged phenyl iodide as a recyclable mediator-electrolyte system for electrosynthesis

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Introduction

Herein we present a new bifunctional mediator (see species **1** in Figure 1), which combines the advantages of indirect electrosynthesis with a straightforward recovery and recycling procedure.[1,2] This was achieved by tethering a redox active moiety based on the I⁺/I³⁺ redox couple to a tetraalkylammonium group. The latter one simultaneously renders sufficient ionic conductivity for electrolysis without additional supporting electrolyte. The applicability of the new electrogenerated hypervalent iodine species for synthesis was explored.

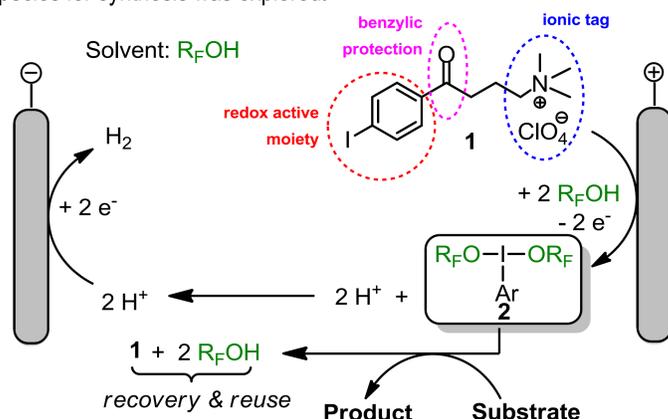


Figure 1. Concept of our electrosynthesis procedure using mediator-electrolyte **1**. R_FOH = fluorinated alcohol.

Electroanalytical studies

Fluorinated alcohols represent the key to the electrochemical generation of hypervalent iodine species due to their high anodic stability and their tendency to stabilize I(III).[3] Therefore, we studied TFE and HFIP as potential solvent candidates using CV. The data shown in Fig. 2 (left) suggests that the use of HFIP is more promising. Conductivity studies reveal that **1** in HFIP allows for electrolysis without addition of supporting electrolyte (top right). The selective formation of a single iodine(III) species was confirmed by ¹H NMR (bottom right) and other techniques.

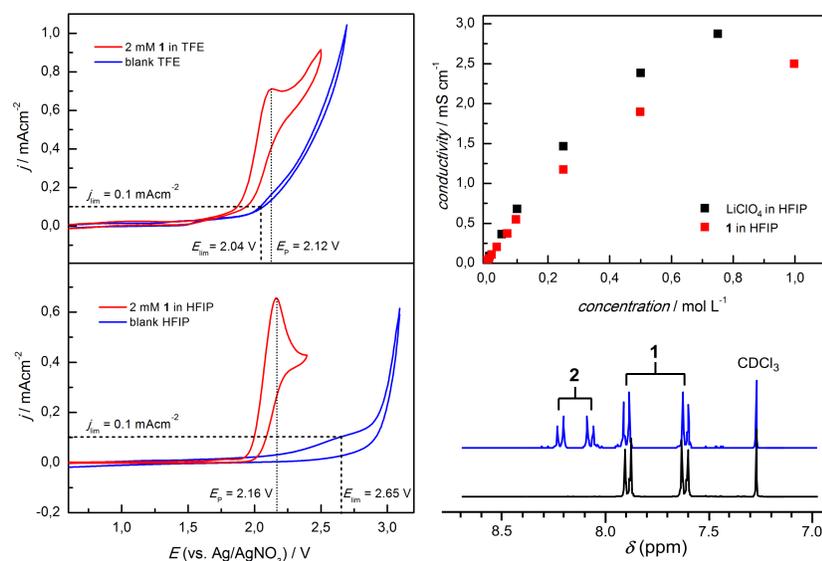
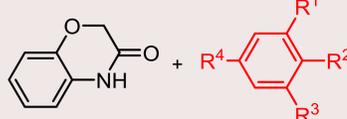
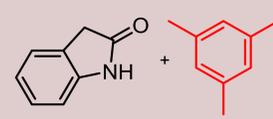
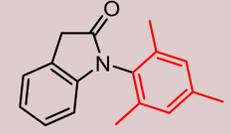
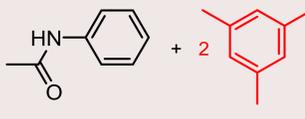
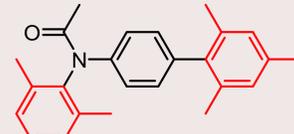


Figure 2. Left: Cyclic voltammetry of mediator **1** in 1,1,1-trifluoroethanol (TFE, top) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, bottom). Top right: Comparison of conductivity of mediator **1** (red squares) in HFIP with LiClO₄/HFIP (black squares). Bottom right: ¹H-NMR spectra of **1** in CDCl₃:HFIP = 5:1 (vol:vol) prior (black line) and after electrolysis (blue line).

Synthetic studies

Applying optimized electrolysis conditions ($j = 15 \text{ mA cm}^{-2}$, WE: glassy carbon, CE: Pt, [1] = 0.2 M in HFIP), a Faradaic efficiency of 80% for the generation of the hypervalent iodine species **2** is possible. The pre-electrolyzed solution of **1** was used for various direct C-C and C-N coupling reactions (see Table 1). After completed reaction, the solvent is evaporated and the remaining mixture is subjected to a solid phase extraction to yield the crude product and analytically pure mediator **1** (typically $\geq 95\%$ recovery), which can be recycled for further runs.

Table 1. Intra- and intermolecular C-N and C-C bond forming reactions using **2** in HFIP.

Starting materials	Products
	 4 examples: 66 - 94%
	 6 examples: 24 - 79%
	 42%
	 75%

Typical reaction procedure: stirring of **2**, amide (1 equiv.) and arene (2 – 10 equiv.) in 10 mL pre-electrolyzed solution (solvent: HFIP) at room temperature, reaction time: 18–24 h.

Conclusion and outlook

- ✓ Development of a new redox-mediator based on the I(I)/I(III) redox couple
- ✓ Elaboration of a green electrosynthetic process: no supporting electrolyte required, straightforward workup and separation, recycling of mediator + solvent
- ✓ Direct oxidative C-N couplings (with H₂ as only byproduct!) between arenes and amides accomplished
- Mechanistic studies and optimization of mediator structure underway
- Further exploration of the reactivity of **2** planned

Acknowledgements

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References:

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- [2] Francke, R.; Little, R. D. *Chem. Soc. Rev.* **2014**, *43*, 2492–2521.
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